

VOLUME 77

SEPARATE No. 85

PROCEEDINGS

AUG 30 1951
AMERICAN SOCIETY
OF CIVIL ENGINEERS
115 South Avenue
ROCHESTER 4, N.Y.

AUGUST, 1951



RESINOUS ION EXCHANGERS IN WATER TREATMENT

By William W. Aultman, M. ASCE

SANITARY ENGINEERING DIVISION

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Printed in the United States of America*

Headquarters of the Society
33 W. 39th St.
New York 18, N.Y.

PRICE \$0.50 PER COPY

1620.6

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AMERICAN SOCIETY OF CIVIL ENGINEERS

Founded November 5, 1852

PAPERS

RESINOUS ION EXCHANGERS IN
WATER TREATMENT

BY WILLIAM W. AULTMAN,¹ M. ASCE

SYNOPSIS

Resinous exchangers are rapidly assuming a place of ever greater importance in the field of water conditioning for municipal and industrial purposes. Whereas the more familiar greensands and synthetic zeolites were useful only for removal of hardness and other metallic ions from water, the newer cation exchangers and anion exchangers of the resinous type provide a means of securing any degree of mineral removal up to complete demineralization of a water. The paper describes the application of resinous cation exchangers to water softening, boiler water treatment, process water treatment, and demineralization of brackish water, and discusses costs of several types of treatment.

INTRODUCTION

In 1850 J. T. Way,² consulting chemist to the Agricultural Society of England, discovered that some soils had the ability to retain the "base," or positive radical, of solutions passing through them while the "acid," or negative radical, passed through unaltered. This appears to be the first recorded case of ion exchange.³ Mr. Way's discovery was an example of base exchange (cation exchange), as he called it. Since that time many other cation exchangers have been found, and materials having anion exchange (acid exchange) properties have been discovered and developed.

This paper will show how the developments in the field of ion exchange may influence the present concepts of water treatment.

THE MEANING OF ION EXCHANGE

Ion exchange may be defined as a reversible interchange of ions between a liquid phase and a solid body. This exchange does not involve any radical

NOTE.—Written comments are invited for publication; the last discussion should be submitted by February 1, 1952.

¹ Water Purification Engr., Metropolitan Water Purification District of Southern California, La Verne, Calif.

² "The Capacity of Soils to Absorb Manure," by J. T. Way, *Journal*, Royal Agricultural Society, Vol. 11, 1850, p. 313.

³ "Ion Exchange," by H. C. Walton, *Journal of Chemical Education*, Vol. 23, 1946, p. 454.

change in the solid structure.⁴ The ion exchanger, or solid body, must have ions of its own to exchange for others, and it must also have a highly porous structure or large exposed surface to allow these ions to move in and out freely. These characteristics were found to be present in the zeolite minerals, a group defined as

"Any of a family of hydrous silicates, * * * so called because many species intumescence before the blowpipe * * * In composition they are analogous to feldspars, their chief metals being aluminum, sodium, potassium, and calcium."⁵

Because of cation exchange phenomena were identified for so many years with the zeolites; the term "zeolite" has been used by many persons to include all ion exchange materials. Today cation exchange softening of water is generally referred to as zeolite softening. This is not strictly correct and, with the advent of the organic exchangers, an effort is being made to identify such softening reaction as cation exchange softening. Similarly when anion exchangers are being used such identification is also necessary.

TABLE 1.—CLASSIFICATION OF ION EXCHANGERS

CATION EXCHANGERS		ANION EXCHANGERS	
Inorganic	Organic	Inorganic	Organic
Natural zeolite (greensand) Processed greensand Synthetic zeolite	Natural (the lignites) Sulfonated coal (carbonaceous "zeolite") Synthetic resins Phenolic base Polystyrene base	Metallic oxides	Synthetic resin

The two classes of ion exchangers, the cation exchangers and the anion exchangers, include both inorganic and organic materials.⁶ A general classification of ion exchangers is given in Table 1. Both inorganic and organic anion exchangers have been produced, but only the organic anion exchangers are widely used because the inorganic materials do not have good operating characteristics for deionization application.

In general all of the cation exchangers may be regenerated with common salt (sodium chloride) and thus be used to remove hardness forming calcium and magnesium from solutions. The organic cation exchangers may also be regenerated with dilute acid solutions and in the resulting hydrogen condition they will remove all metallic cations (sodium, potassium, calcium, magnesium, iron, copper, and manganese) from solution. The anion exchangers, used to remove the acid ions (sulfates, chlorides, and nitrates) from solution, may be regenerated with either soda ash (sodium carbonate), caustic soda, or ammonia.

⁴ "Ion Exchange Between Solids and Solutions," by Harold Frederic Walton, *Journal*, The Franklin Institute, Vol. 232, 1941, p. 306.

⁵ "Webster's New International Dictionary," G. & C. Merriam Co., Springfield, Mass., 2d Ed., 1942.

⁶ "High-Capacity Cation Exchangers," by F. K. Lindsay, *Journal*, American Water Works Association, Vol. 42, January, 1950, p. 75.

DEVELOPMENT OF ION EXCHANGE PROCESSES

The Cation Exchangers.—The lime and lime-soda ash methods of water softening can be dated before 1850⁷ and these methods have widespread application in industrial and municipal water treatment plants throughout the world. With the introduction of the zeolites early in the 20th century, cation exchange softening was initiated.

It was around 1900 that the first industrial water softening plant using natural greensand as the cation exchanger was put into service in Europe. The first municipal zeolite plant was placed in operation in the United States in 1923, at Wyomissing, Pa.⁸ Since that time higher capacity cation exchangers have been developed including the processed greensands, synthetic siliceous zeolites, carbonaceous exchangers, and the resinous exchangers. The relative exchange capacities of these various materials are given in Table 2.

Since they were first introduced commercially, the cation exchangers have held a major place in both industrial and municipal water treatment. At first they were used in water softening only for calcium and magnesium removal. Then it was found that iron and manganese could be removed from water by some of the inorganic exchangers, with manganous sulfate and potassium permanganate used as regenerants, or by the organic exchangers with acid as a regenerant. Many industrial installations used cation exchangers for boiler water treatment, because the water thus produced had zero hardness and did not tend to form a hard scale. However, silica is not removed from the water by this treatment; in fact it is often increased by passing through the siliceous zeolites, and the silica can cause trouble in high pressure boilers.

Over 700 municipalities have installed cation exchange materials in their domestic treatment plants. After thorough investigation the Metropolitan Water District of Southern California (hereinafter called "the District") determined that the lime-zeolite method of treatment was the most economical to use in the 100 mgd water softening plant placed in service in 1941. This plant, doubled in capacity in 1949,^{9,10} still utilizes the cation exchangers for softening

TABLE 2.—RELATIVE EXCHANGE CAPACITY OF CATION EXCHANGERS

Cation exchanger (1)	Nominal exchange capacity (grains per cubic foot) (2)	REGENERATIVE SALT DOSAGE	
		Volumetric ^a (3)	Effective ^b (4)
Greensand.....	2,800	1.26	0.45
Processed greensand.....	5,500	2.47	0.45
Synthetic siliceous zeolite.....	11,000	4.95	0.45
Carbonaceous.....	7,000	3.15	0.45
Resin, phenolic.....	15,000	6.75	0.45
Resin, polystyrene.....	28,000	12.60	0.45
Resin, polystyrene.....	20,000	5.00	0.25

^a Pounds of salt per cubic foot of exchanger. ^b Pounds of salt per kilograin of hardness removed.

⁷ "Water Supply and Treatment," by C. P. Hoover, National Lime Association, Washington, D. C.

⁸ "Review of Performance of Municipal Zeolite Plants," by H. M. Olson, Ohio Salt Company, Wadsworth, Ohio.

⁹ "Metropolitan Water District Doubles Capacity of La Verne Softening and Filtration Plant," by R. B. Diemer, *Civil Engineering*, Vol. 19, 1949, p. 669.

¹⁰ "World's Largest Water Softening Plant," by William W. Aultman, *Water and Sewage Works*, Vol. 96, 1949, p. 456.

and is the largest zeolite process softening plant in the world with a total of 56,700 cu ft of cation exchanger installed.^{11,12}

Resinous Exchangers.—The progress that has been mentioned in the application of the cation exchangers is based primarily on the use of the siliceous or carbonaceous type of exchanger. The advent of the resinous type exchangers introduces an entire new field of use and efficiency and requires a complete re-evaluation of the treatment processes.

The development of the resinous exchangers was first reported by the English scientists B. A. Adams and E. L. Holmes in 1935.¹³ Four years later the commercial production of these resins was started in the United States. Since that time the development of cation and anion resinous exchangers has been phenomenal. It is believed that the potentialities of these resins are just beginning to be realized.

In addition to the use of the ion exchangers in the water treatment field, the new resinous exchangers are being used extensively in the chemical process industries with an evergrowing field of application. For example, the inorganic ash may be eliminated from sugar juice by passing the juice through a cation-anion treatment plant, thereby materially increasing the yield of crystallizable sugar and reducing evaporator scale and operating difficulties. Small concentrations of the metallic ions, such as copper, nickel, aluminum, etc., may be recovered from solution in more concentrated form by use of an organic exchanger with a regenerant of the desired properties. The resinous exchangers have been used for: (a) the treatment of milk for curd modification; (b) the treatment of whey for the recovery of lactose; (c) the purification of formalin; (d) the refining of hydrocarbons; (e) the purification of polyalcohols; (f) the separation of inorganic cations; and other uses too numerous to mention.¹⁴ This paper, however, will deal only with their use in water treatment.

APPLICATION OF RESINOUS EXCHANGERS IN WATER SOFTENING

The chemical treatment of water, other than for sterilization or coagulation, is usually undertaken for three general purposes: (1) softening of water for domestic and industrial use; (2) boiler water conditioning; and (3) process water preparation. Under the two latter main headings may fall a number of subheadings depending on the quality of the raw water, the boiler water pressure encountered, and the requirements of the process industry. What is the place of the new resinous exchangers in these three phases of water treatment?

The high-capacity polystyrene resinous exchangers have three major characteristics that cause them to be given special consideration when determining the type of exchanger to use for water softening.

First, their high capacity permits a smaller volumetric installation, with corresponding smaller equipment cost, for a softening capacity equal to any of the other exchangers.

¹¹ "Use of Organic Cation Exchangers for Municipal Water Softening," by W. W. Aultman and A. E. Bowers, *Proceedings, 9th Annual Water Conference, Engineers' Society of Western Pennsylvania*, 1948, p. 1.

¹² "Cation Exchangers for Municipal Water Softening," by Lee Streicher and A. E. Bowers, *Journal, American Water Works Association*, Vol. 42, January, 1950, p. 81.

¹³ "Absorptive Properties of Synthetic Resins," by B. A. Adams and E. Leighton Holmes, *Journal of the Society of Chemical Industry*, Vol. 54, 1935, p. 1T.

¹⁴ "Ion Exchange," by Robert Kienin, *Industrial & Engineering Chemistry*, Vol. 42, 1950, p. 65.

Second, if the water being softened is clear, its quality in other respects has, almost without exception, no deleterious effect on the nonphenolic exchangers. They are not affected by a pH within the range of 1 to 14, or a temperature of more than 200° F, and the chemical composition of the water does not tend to break down the exchanger. This is not true of the siliceous synthetic zeolites that should be operated within a pH range of 6.0 to 8.3, at temperatures not exceeding 140° F, and will be dissolved slowly by waters low in silica.

Third, the operating efficiency of the polystyrene resin is appreciably higher than any other type of exchanger in commercial use.

In actual operation of the District plant every attempt is made to operate the exchangers as efficiently and economically as possible. For the synthetic siliceous zeolites an average exchange capacity of 8,700 grains per cu ft is obtained at a regeneration salt requirement of 0.37 lb of salt per kilograin of hardness removed. The polystyrene resins, on the other hand, have a capacity of 22,000 grains per cu ft when regenerated at the rate of 0.24 lb of salt per kilograin of hardness removed. Thus, in comparison with the synthetic siliceous zeolite, the polystyrene resins show 2.5 times the exchange capacity with only $\frac{2}{3}$ the salt consumption per kilograin of hardness removed.

What does this mean in dollars and cents? For example, the Colorado River water, as received at the District softening plant, had an average hardness in 1950 of 321 ppm or 18.8 grains per gal. Salt costs the District \$4.46 per ton delivered (1950). To soften 1,000,000 gal of this water to zero hardness with zeolite requires 6,956 lb of salt (costing \$15.51) although it requires only 4,512 lb of salt (costing \$10.06) when a polystyrene resin is used. The resulting net saving is \$5.45 per million gallons. If the salt cost \$9.00 a ton, or more, as it does at most places in the United States, the saving would exceed \$11.00 per million gallons. This is a saving in salt alone and does not include savings in rinse water quantities or lower equipment cost.

The saving in salt, however, is offset to some extent by the increased cost of the resin. The relative cost of zeolite and polystyrene resinous exchanger is approximately proportional to the exchange capacity of the two materials, the cost of the resin being about 2.5 times that of the zeolite. But the useful life of the two exchangers is not equal. Under identical operating conditions, using Colorado River water, the life of zeolite is found to average about 2,000,000 per cu ft of exchanger whereas the life of the polystyrene resin is in excess of 5,000,000 gal per cu ft of exchanger. With all factors considered, an appreciable saving is shown by the use of the polystyrene exchanger, rather than zeolite.

For those cities located near the ocean another possibility of reducing the cost of treatment is available by using the polystyrene resin with ocean water as the regenerant. Although this is not a new scheme (there are several zeolite plants now using sea water for regeneration), it is the first time that relatively high-capacity exchange has been available and is obtainable with a small amount of sea water circulation. A new plant at Ventura, Calif., uses sea water for regeneration. The exchange capacity of the resin at various dosages of sea water for regeneration is shown in Fig. 1. It is evident that exchange

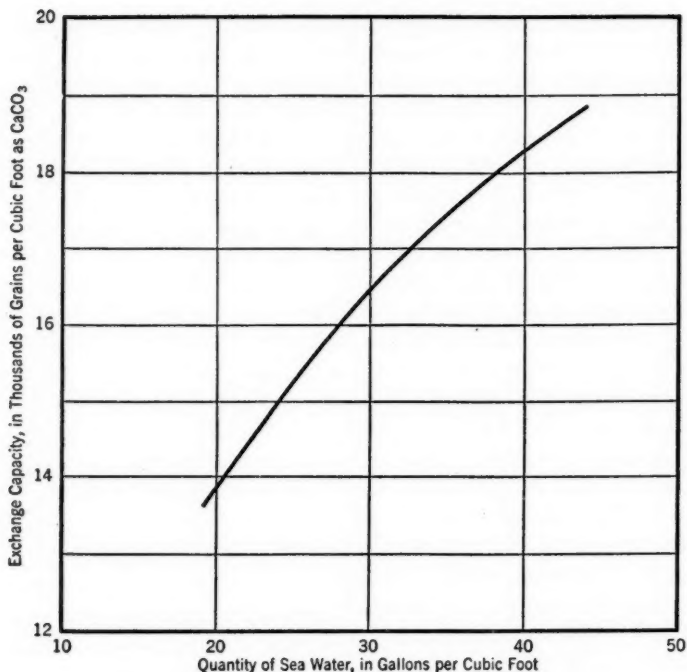


FIG. 1.—EFFECT OF SEA WATER REGENERATION ON THE OPERATING EXCHANGE CAPACITY OF A POLYSTYRENE RESIN.

capacities in excess of those obtained from any inorganic exchanger are possible with this polystyrene resin under these conditions.

RESINOUS EXCHANGERS IN BOILER WATER TREATMENT

The factors pertaining to the use of the resinous exchangers for municipal water softening are likewise true for water softening in connection with boiler water conditioning. However, there are additional factors in boiler water treatment, particularly in high pressure boilers, that must be considered.

Boilers require a water low in silica, but the true zeolites, either natural or synthetic, are siliceous materials. Water passing through these zeolites tends to pick up silica, the degree of pickup depending upon the silica content, temperature, pH, and other characteristics of the water. This silica pickup is so great at times that municipal plants for treatment of domestic water have added silica to the raw water to protect the zeolite.¹⁵ Carbonaceous exchangers have been extensively used for boiler water treatment to avoid the introduction of silica from siliceous materials. This, likewise, is an advantage of the resinous exchangers. With the highly basic resinous anion exchangers available, silica may be removed from water, and this is an important forward step in the processing of boiler waters.

¹⁵ "Operating Characteristics of Synthetic Siliceous Zeolite," by L. Streicher, H. E. Pearson, and A. E. Bowers, *Journal, American Water Works Association*, Vol. 39, 1947, p. 1133.

The ability of the resinous cation exchangers to withstand temperatures in excess of 200° F makes them suitable for use in plants in which hot water is processed for boiler feed purposes in order to conserve heat.

At times it may be desirable to partly or wholly demineralize the water used in a boiler. This can be accomplished with the resinous cation and anion exchangers whose operation will be described subsequently.

USE OF RESINOUS EXCHANGERS FOR PROCESS WATER TREATMENT

Many process industries require a very pure or a very uniform quality of water. When low salinity water has been required in the past, distillation units have usually been employed. With the advent of the organic cation and anion exchangers a water equal in quality to distilled water can be produced, generally at a lower cost.

In the demineralization process, water is passed through an organic cation exchanger that has been regenerated with dilute acid, that is, a unit operating on the hydrogen cycle. In this unit all of the cations in the water (calcium, magnesium, sodium, potassium, and dissolved iron and manganese) are absorbed on the exchange material, and hydrogen ions are released from the resinous exchangers. The water is then passed through an anion exchanger unit where the negative ions in the water (chlorides, sulfates, and nitrates) are absorbed on the exchanger and the carbonate or hydroxyl ions are released, depending upon whether soda ash or caustic soda is used for regenerating. The resultant water consists essentially of H_2O and CO_2 . The carbon dioxide (CO_2) may be removed by aeration, leaving a pure water. Recently developed resins, operating in suitably designed equipment have produced demineralized water having a specific electrical resistance of between 10,000,000 and 20,000,000 ohms per cu cm. This compares with good quality distilled water with a resistance of 500,000 to 1,000,000 ohms per cu cm. The chemical purity of the water is proportional to its electrical resistance, 1 ppm of $CaCO_3$ salinity in water representing a specific resistance of about 460,000 ohms.

The cost of demineralization is directly proportional to the salinity of the water being treated. The cost of distilled water, however, is affected very little by the quality of water being used, except for the production of scale within the distillation unit. At the chemical prices prevailing in the California area the cost of demineralizing a water containing 400 ppm total dissolved salines is about \$0.30 per 1,000 gal. The cost of distilling such water is from five to ten or more times this cost, depending upon the type of distillation equipment being used and its size. As the salinity of the water being treated increases, the cost of demineralization increases proportionately, until a point is reached where demineralization by means of the resinous cation and anion exchangers becomes greater than the cost by distillation methods.

From the foregoing discussion it is evident that a water of almost any quality desired may be produced by the resinous cation exchangers operating on either the sodium or the hydrogen cycle coupled with the resinous anion exchangers. This gives the sanitary or chemical engineer an excellent tool to use in solving some of the intricate problems of water quality presented by many of the process industries.

DEMINERALIZATION OF BRACKISH AND SEA WATERS

With the publicity given the advances in the science of demineralization many laymen seem to think that it is a simple and inexpensive matter to produce a potable water from brackish or salt waters. Where cost is not a consideration it must be admitted that the demineralization of sea water is a possibility. A cost of \$5.00 per pint for drinking water produced from sea water by special ion exchangers aboard life rafts during World War II was inconsequential when it meant saving men's lives. But the cost of demineralizing water for municipal or industrial use must compare favorably with the cost of local sources of supply to be given serious consideration.

Considerable research on the partial demineralization of the brackish waters of Palestine¹⁶ developed a new, cheaper method of operation for large-scale treatment of waters containing from 1,000 ppm to 2,500 ppm total dissolved salines, enabling the production of a potable water of 300 to 500 ppm total salines. This is accomplished by using counterflow of water and regenerant solutions with lime as the anion exchange regenerant. Lime regeneration has been tried on pilot plant scale only, but it appears to operate satisfactorily. With this method of treatment it appears possible to produce a water suitable for domestic use at a cost that is within the realm of economic feasibility, if the natural water contains no more than about 2,500 ppm total dissolved salines.¹⁷

Unfortunately, sea water contains from 32,000 to 36,000 ppm total salines, and to produce a potable water from this source with the established methods of demineralization would cost about \$25.00 per 1,000 gal for chemicals alone (1950). Vapor compression distillation is much cheaper than demineralization of sea water, but with the equipment available water so produced would still cost over \$1.25 per 1,000 gal when all factors are taken into consideration.^{18,19} Perhaps more efficient means of producing potable water from sea water may evolve if Congress authorizes appropriations for research on this problem, but available scientific knowledge does not indicate that the cost of such reclaimed water can ever approach that of locally developed water supplies within the United States.

SUMMARY

The development of the new resinous cation and anion exchangers may influence the present concepts of water treatment in the following respects:

a. Waters of almost any desired quality may be produced for municipal and industrial use with the economic feasibility of treatment depending upon the quality of the raw water being treated.

b. The quality of the water being treated has little or no effect on some of the resinous exchangers, a factor of considerable value in water conditioning for boilers and the process industries.

¹⁶ "Ion Exchange Process for Brackish Waters," *Chemical and Engineering News*, Vol. 27, 1949, p. 3306.

¹⁷ Private communication from Ionics, Inc., Cambridge, Mass., January 11, 1950.

¹⁸ "Fresh Water from Salt," by W. W. Aultman, *Engineering and Science Monthly*, Vol. XII, 1949, p. 3.

¹⁹ "Desalting Sea Water for Domestic Use," by William W. Aultman, *Journal, American Water Works Association*, Vol. 42, August, 1950, p. 786.

c. Because of their high salt efficiency, the polystyrene resins operating on the sodium cycle will warrant serious consideration in any studies to determine the best method of softening any specific water.

d. Silica may be removed from water with comparative facility and at a reasonable cost.

The development of the resinous ion exchangers is in its infancy, and all engineers in any way concerned with water treatment when using these materials should keep abreast of the progress made in the perfection of operating techniques and procedures.

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